LETTER

Reply to Wallington et al.: Differences in electronic structure of global warming molecules lead to different molecular properties

The comment by Wallington et al. (1) is not germane to our studies (2, 3), contributes to further confusion on the use of the radiative forcing (RF) and radiative efficiency (RE) terms, and misses a fundamental point: differences in electronic structure lead to different molecular properties.

In the atmospheric sciences literature, the terms RF and RE often are used incorrectly and sometimes interchangeably (4, 5). RF refers to the change in the net irradiance at the tropopause over a time period and requires use of a radiative transfer model. RE refers to the change in irradiance solely based on a species' infrared (IR) spectrum, which assumes a constant atmospheric concentration at all altitudes.

The global warming potential (GWP) of a molecule is a function of its RF and atmospheric lifetime (6). Molecular RF is a function of the molecular RE and atmospheric conditions. Central to a molecule's RE is its IR absorption cross-section. The IR absorption cross-section can be experimentally measured or calculated using electronic structure theory and is related to the dipole transition moment for each vibrational mode. It is this fundamental molecular property that allows a direct connection to be made between a molecule's molecular structure and its absorptive capacity. Previous studies failed to identify the relationship between a specific bond dipole and the overall molecular structure. In the studies by Bera et al. (2, 3), a molecular radiative efficiency, or effectiveness of absorption of IR radiation, was developed by means of systematic quantum mechanical calculations. The origin of a large IR absorption for several classes of molecules as well as specific isomers of a given compound was traced to their possessing large dipole derivatives (2), and, subsequently, a design strategy was devised to screen them (3).

Additionally, Wallington et al. (1) use the black body radiation curve for Earth (accounting for atmospheric absorption) to suggest that not all radiation within the IR atmospheric window should be treated equivalently. Of course, this is taken into account when computing an RF quantity (rather than the molecular RE), but the molecules that we study are all trace species in the atmosphere; thus, their entire absorption within the IR window should be taken into account because, by definition, IR absorption within this energy range is not saturated by the Earth's atmosphere.

Finally, Wallington et al. (1) suggest that the only important molecular property when computing a GWP is its atmospheric lifetime. However, reducing the climate impact for a molecule by as much as a factor of 2 is certainly important, which we showed occurs when comparing the molecular IR absorption of structural isomers of partially fluorinated species. Also, depending on the industrial application, it is not always possible to use a compound that has a short atmospheric lifetime. Furthermore, our studies show that the electronic structure of structural isomers of partially fluorinated compounds is very different, particularly the polarity of bonds. Therefore, our studies suggest that the atmospheric lifetimes of structural isomers could be very different, because rate constants for reaction with OH radical could vary significantly.

***Partha P. Bera*[a], *Joseph S. Francisco*[b], *and Timothy J. Lee*[a,1]**

[a]*Space Science and Astrobiology Division, National Aeronautics and Space Administration Ames Research Center, Moffett Field, CA 94035; and* [b]*Departments of Chemistry and Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907-1393*

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The authors declare no conflict of interest.

[1]To whom correspondence should be addressed. E-mail: Timothy.J.Lee@nasa.gov.